

**GLOBAL OCEAN SURFACE WATER PARTIAL PRESSURE OF CO₂ DATABASE:
MEASUREMENTS PERFORMED DURING 1957–2009
(Version 2009)**

Contributed by
Taro Takahashi and Stewart C. Sutherland

Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY 10964

Date Published: September 2007
Date Updated: June 2010

Prepared for the Climate Change Research Division
Office of Biological and Environmental Research
U.S. Department of Energy
Budget Activity Numbers KP 12 04 01 0 and KP 12 02 03 0

Prepared by
Alex Kozyr

Carbon Dioxide Information Analysis Center
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6335
managed by
UT-BATTELLE, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

List of Figures.....	v
List of Tables	v
Abbreviations and Acronyms	vii
Abstract.....	ix
1. INTRODUCTION	1
2. OBJECTIVE.....	2
3. SUMMARY OF ADDITIONS AND CORRECTIONS IN VERSION 2008	2
4. METHODS OF COMPUTATION	3
5. QUALITY CONTROL.....	4
6. DATA SOURCES.....	5
7. DATA LISTING.....	7
8. HOW TO OBTAIN THE DATA AND DOCUMENTATION	8
9. ACKNOWLEDGEMENTS.....	9
10. REFERENCES	9

LIST OF FIGURES

1	Location of LDEO V2009 master database of sea surface pCO ₂ observations.	2
---	---	---

LIST OF TABLES

1	List of data contributors to the global surface water pCO ₂ LDEO database	6
2	Data elements listed in the master data file “LDEO_databaseV2009.txt”	7
3	Data elements listed in the metadata file “LDEO_Database_Metadata_V2009.xls”	8

ABBREVIATIONS AND ACRONYMS

AOML	Atlantic Oceanographic and Meteorological Laboratory
CDIAC	Carbon Dioxide Information Analysis Center
CLIVAR	Climate Variability (Program)
CO ₂	carbon dioxide
CSIRO	Australian Commonwealth Scientific and Research Organization
DOE	U.S. Department of Energy
FTP	file transfer protocol
f CO ₂	fugacity of CO ₂
GEOSECS	Geophysical Sections Experiment
IGY	International Geophysical Year
JGOFS	Joint Global Ocean Flux Study
LDEO	Lamont-Doherty Earth Observatory
NCAR	National Center for Atmospheric Research
NCEP	National Centers for Environmental Prediction
NDP	numeric data package
NOAA	National Oceanic and Atmospheric Administration
NSF	National Science Foundation
ORNL	Oak Ridge National Laboratory
pCO ₂	partial pressure of CO ₂
PMEL	Pacific Marine Environmental Laboratory
SSS	sea surface salinity
SST	sea surface temperature
VOS	Volunteer Observing Ship
WOCE	World Ocean Circulation Experiment

ABSTRACT

Takahashi, T., S.C. Sutherland, and A. Kozyr. 2010. Global Ocean Surface Water Partial Pressure of CO₂ Database: Measurements Performed During 1957–2009 (Version 2009). ORNL/CDIAC-152, NDP-088(V2009). Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, doi: 10.3334/CDIAC/otg.ndp088(V2009).

Approximately 4.75 million measurements of surface water partial pressure of CO₂ obtained over the global oceans during 1957–2009 are listed in the Lamont-Doherty Earth Observatory (LDEO) database, which includes open ocean and coastal water measurements. The data assembled include only those measured by equilibrator-CO₂ analyzer systems and have been quality-controlled based on the stability of the system performance, the reliability of calibrations for CO₂ analysis, and the internal consistency of data. To allow re-examination of the data in the future, a number of measured parameters relevant to pCO₂ measurements are listed. The overall uncertainty for the pCO₂ values listed is estimated to be $\pm 2.5 \mu\text{atm}$ on the average.

For simplicity and for ease of reference, this version is referred to as 2009, meaning that data collected through 31 December 2009 has been included. It is our intention to update this database annually. There are 42 new cruise/ship files in this update. In addition, some editing has been performed on existing files so this should be considered a "V2009" file. Also we have added a column reporting the partial pressure of CO₂ in seawater in units of Pascals.

The data presented in this database include the analyses of partial pressure of CO₂ (pCO₂), sea surface temperature (SST), sea surface salinity (SSS), pressure of the equilibration, and barometric pressure in the outside air from the ship's observation system.

The global pCO₂ data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center (CDIAC). The NDP consists of the oceanographic data files and this printed documentation, which describes the procedures and methods used to obtain the data.

Keywords: carbon dioxide, partial pressure of CO₂, global carbon cycle, global ocean, equilibrator-CO₂ analyzer systems.

1. INTRODUCTION

Transfer of CO₂ between the atmosphere and the oceans is a critical process of the global carbon cycle and is important for the future of the earth's climate. During the past decade, about 6 Pg-C yr⁻¹ [1 Pg (peta grams) = 10¹⁵ grams = 1 Giga ton] has been emitted into the atmosphere from various anthropogenic sources including the combustion of fossil fuels, cement production, deforestation, land use changes, and others. On the basis of various independent scientific methods including changes in oxygen and CO₂ concentrations in the atmosphere (Keeling et al. 1996, Bender et al. 2005, Garcia and Keeling 2001), sea-air differences in CO₂ partial pressure (Takahashi et al. 2002, Takahashi et al., 2009), distribution of carbon isotopes (¹²C, ¹³C, and ¹⁴C) (Quay et al. 2003), ocean CO₂ inventories (Sabine et al., 2004), inversion of atmospheric CO₂ distribution data using atmospheric circulation models (Patra et al. 2006, Baker et al., 2006), and various global carbon cycle models (Sarmiento et al. 2000, Gruber and Sarmiento 2002), the annual uptake rate of CO₂ by the oceans has been estimated to be about 2 Pg-C yr⁻¹ for the past decade. Thus, ~30% of the anthropogenic CO₂ emissions are absorbed annually by the oceans, and ~50% remain in the atmosphere. As a result, the atmospheric CO₂ concentration is increasing at a mean rate of about 1.5 ppm yr⁻¹ (or 0.4% per year), and the concentration of CO₂ dissolved in surface ocean waters is also increasing, causing the acidification of ocean waters. Accurately documenting changes in the CO₂ chemistry in ocean waters over time is therefore important for understanding the fate of anthropogenic CO₂ released into the atmosphere as well as charting the future course of atmospheric CO₂ levels that would affect the earth's climate.

Carbon dioxide molecules react chemically with water to form bicarbonate (HCO₃⁻) and carbonate (CO₃⁼) ions, neither of which communicate with the overlying air. Only about 0.5% of the total CO₂ molecules dissolved in seawater communicate with air via gas exchange across the sea surface. This quantity is called the partial pressure of CO₂ (pCO₂), which represents the CO₂ vapor pressure. The seawater pCO₂ depends on the temperature, the total amount of CO₂ dissolved in seawater, and seawater pH. Over the global ocean, it varies from about 100 µatm to 1000 µatm (1 µatm = 10⁻⁶ atm). When seawater pCO₂ is less than the atmospheric pCO₂ (presently about 380 µatm), seawater takes up CO₂ from the overlying air; when it is greater than the atmospheric pCO₂, it emits CO₂ to the air. The rate of transfer of CO₂ across the sea surface is estimated by: (sea-air CO₂ flux) = (transfer coefficient) x (sea-air pCO₂ difference). The transfer coefficient depends primarily on the degree of turbulence near the interface, and is commonly expressed as a function of wind speed. Since the time-space variation for atmospheric pCO₂ is much smaller than that for surface ocean water pCO₂, the magnitude of sea-air CO₂ flux is governed primarily by seawater pCO₂. Therefore, the inter-annual and seasonal variability for surface water pCO₂ is of particular interest.

The atmospheric CO₂ concentrations observed at a number of locations over the globe is summarized in GLOBALVIEW-CO2 (2006) and TRENDS ON LINE (2006). On the other hand, no single data file for surface water pCO₂ that includes long-term and global coverage has been made accessible to the general public. About 20 years ago, we started to assemble a global surface water pCO₂ data for time-space variability studies for the global oceans using the observations made by the Lamont-Doherty Earth Observatory (LDEO) group. Many investigators from other institutions contributed data to the database for the first publication on the global ocean pCO₂ and sea-air CO₂ flux (Takahashi et al. 1997), which was based on about 0.25 million pCO₂ measurements; the second publication (Takahashi et al. 2002) was based on about a million measurements. The LDEO database now consists of more than 4.7 million pCO₂ measurements (Fig. 1) plus a number of other measured supporting parameters. A paper summarizing these observations has been submitted for publication in the Deep Sea Research (Takahashi et al. 2009). A subset of this database is used for estimating the sea-air CO₂ flux from coastal waters surrounding North America (Chavez and Takahashi 2007). Mindful of the increasing importance of CO₂ studies for future global welfare, LDEO is sharing this data file widely with the global research

communities and the public through the Carbon Dioxide Information Analysis Center (CDIAC) data archive.

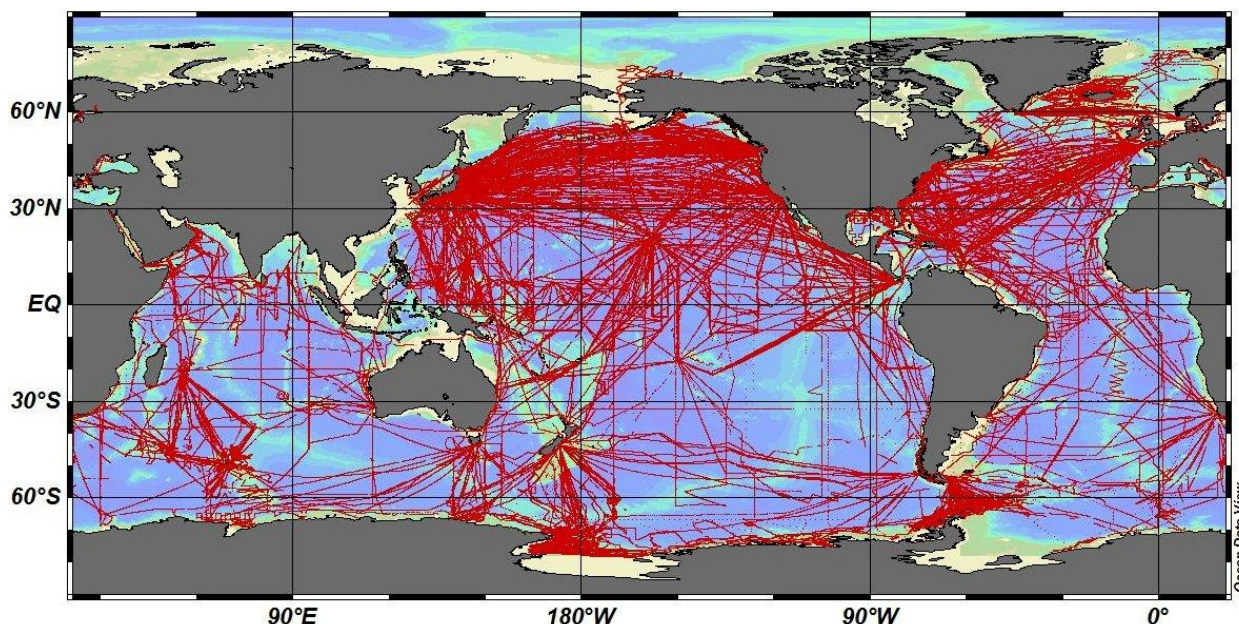


Fig. 1. Location of LDEO V2009 master database of sea surface pCO₂ observations.

2. OBJECTIVE

Modern investigation of ocean water pCO₂ started during the International Geophysical Year (IGY), 1957–1960, with the introduction of infrared CO₂ gas analyzer and gas-water equilibrators aboard oceanographic research vessels (Takahashi, 1961; Keeling et al., 1965; Keeling, 1965; Broecker and Takahashi, 1966; Keeling and Waterman, 1968; Keeling, 1968). Combined with high-accuracy CO₂-air-gas mixtures made available for the calibrations of the analyzers at sea, the quality of seawater pCO₂ data was greatly improved from that obtained in the pre-World War II era. During major oceanographic programs that took place after IGY, the CO₂ analyzers and equilibrators have been steadily improved to give more frequent observations and better accuracy, although the principles of the measurement remained essentially unchanged. Computers used for system control and data logging contributed significantly to the data quality. The objective of this database is to assemble high-quality pCO₂ data obtained using the equilibrator-analyzer method, and to reprocess the data using a standardized method of computation, that will be described below. Therefore, the pCO₂ values listed in this database may differ from the original listings prepared by respective investigators.

3. SUMMARY OF ADDITIONS AND CORRECTIONS IN VERSION 2009

This version is referred to as Version 2009, and includes the data collected through 31 December 2009. In this update, 42 new cruise/ship files are added to the previous version 2008 (see NDP-088r) including several files for the IGY expeditions in 1957–1963. Four files were received from Dr. Ralph F. Keeling at Scripps Institute of Oceanography containing the data from the late Dr.

Charles D. Keeling's work on the “1957 *Downwind*” and “1961 *Monsoon*”, “1962 *Lusiad*” and “1963 *Lusiad*” Expeditions, re-edited by Lee Waterman, one of the original investigators, to improve their accuracy (Waterman et al., 2006-a, -b, -c and -d. See references for URL). The other file is for the 1957–1958 R/V *Vema* Expedition by Takahashi (1961). Based on his independent calibrations, he reported a mean atmospheric CO₂ value (in dry air) of 315.3 ± 1.4 ppm (N = 28) over the Atlantic Sector of the Southern Ocean (51°S-57°S; 41°W-02°E) during March 4-24, 1958. C. D. Keeling reported a mean value of 314.1 ppm for March, 1958, at the South Pole Station, and 0.3 ± 0.1 ppm higher values at the Palmer and Amsterdam Island stations. These data sets are in agreement within their respective uncertainties, and therefore, no adjustment was made for the CO₂ values for gas samples equilibrated with seawater. All these data are reprocessed in a manner described below to maintain the consistency with the data in this database.

4. METHODS OF COMPUTATION

The seawater pCO₂ data listed in LDEO database are based on direct measurements of seawater pCO₂ made using equilibrator-CO₂ analyzer systems. Many of the data listed are from semi-continuous pCO₂ systems with flow-through water; many others are measurements for discrete water samples made at hydrographic stations along with measurements for other chemical and physical properties. Although different types of equilibrators (e. g., shower type, bubbling type, membrane type, and rotating disks in flow-through or closed circulation systems) and CO₂ gas analyzers (non-dispersive infrared analyzers and gas chromatographs of various designs) were employed, the results from different systems are accepted as long as analyzers were properly calibrated using validated CO₂-air gas mixtures and the carrier gas was equilibrated with seawater samples. Because of the diversity of methods used, it is impossible to present details of the method used by each contributing research group. Detailed methodology may be obtained directly from the investigators listed in Table 1, or from the CDIAC reports for specific expeditions.

It is important to point out that the methods used for computing CO₂ concentrations in equilibrated gas have been varied among groups. For example, some groups computed a least-square fit of readings for three or more standard gas mixtures to a quadratic equation and used it to calculate concentrations in samples. Some groups used four or five standard gas mixtures for calibrations, and fitted the data to a 4th order polynomial equation. And some groups used an output from linearization circuits of infrared analyzer, and linearly regressed three or more standard gas readings to obtain sample CO₂ concentrations. The outputs from a gas chromatograph are a linear function of CO₂ concentration, and hence a linear regression was used for calibration. These different data reduction methods yield CO₂ concentrations varying ± 1.5 ppm (or ± 1.5 μ atm in pCO₂). However, we did not recompute the CO₂ values using a single uniform algorithm but instead, accepted CO₂ concentration values as reported to us. Since different analyzers and different numbers of standard gas mixtures were used by respective groups, no single uniform data reduction scheme can be applied, and hence we relied on the judgment of each group for selecting the data reduction scheme most suited for their operational modes and skills. Measurements that were made using only one calibration gas mixture were judged unreliable and were not included in this database.

Using the reported CO₂ concentration values, the pCO₂ value in sample seawater at the equilibration temperature, (pCO₂)_{eq}, has been recomputed with the relationship:

$$(pCO_2)_{eq} = V_{co2} (P_{eq} - P_{water}),$$

where V_{co2} is the mole fraction concentration of CO₂ in carrier gas (V_{co2} is same as X_{CO2} , which is often used in literature, and these qualities may be used interchangeably); P_{eq} is the total pressure of gas in the equilibrator; and P_{water} is the equilibrium water vapor pressure at temperature of equilibration, T_{eq} , and salinity. Since some equilibrators were operated open to the room air, P_{eq} values may be equal to the

ship's interior pressure or to the barometric pressure outside the ship depending on the location of the equilibrator. When an equilibrator is located in an enclosed shipboard laboratory and is open to the room air, P_{eq} is the ambient pressure in the laboratory. While an equilibrator operated in an enclosed space, only the barometric pressure at sea surface was reported in some data sets, but not P_{eq} . In such cases, P_{eq} is assumed to be the reported barometric pressure at sea surface plus 3 mb, that represents an overpressure normally maintained inside a ship. This correction increases the $(pCO_2)_{sw}$ value by about 1 μ atm. When the pressure was not reported, we used the climatological value in the nearest box from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) Reanalysis II Project file for the month of the observation. The pCO_2 at in-situ seawater temperature is computed using an integrated form of the temperature effect for isochemical seawater, $(\partial \ln pCO_2 / \partial T)_{Sal, Alk, TCO_2}$ (Takahashi et al., 1993):

$$(pCO_2)_{sw} @ T_{in situ} = [(pCO_2)_{sw} @ T_{eq}] \text{Exp}\{0.0433 (T_{in situ} - T_{eq}) - 4.35 \times 10^{-5} [(T_{in situ})^2 - (T_{eq})^2]\}$$

where the “sw” and “eq” indicate the in situ and equilibrator conditions respectively. Throughout the computation, CO_2 gas is assumed to behave as an ideal gas that mixes with air and water vapor ideally. Although CO_2 fugacity is used in a number of published papers and data reports, we refrained from using the fugacity since it is computed differently from an investigator to another. Although we do not list the sea-air pCO_2 differences in this report, we recommend the formula below for the computation of atmospheric pCO_2 and the corresponding value for sea-air pCO_2 difference.

$$(pCO_2)_{air} = (V_{CO_2})_{air} (P_{baro} - P_{sw})$$

where P_{baro} is the barometric pressure at sea surface, and P_{sw} is the equilibrium water vapor pressure at the temperature and salinity for mixed layer water. The subscript “air” indicates the value for atmosphere samples.

The sea-air pCO_2 difference, ΔpCO_2 , is then computed using:

$$\Delta pCO_2 = (pCO_2)_{sw} - (pCO_2)_{air}$$

Since CO_2 is assumed to be an ideal gas for both $(pCO_2)_{sw}$ and $(pCO_2)_{air}$, the small effects of non-ideality should cancel due to differencing for ΔpCO_2 . Positive ΔpCO_2 values indicate that the sea is a source for atmospheric CO_2 , whereas negative values indicate that the sea is a sink.

Values for the fugacity of CO_2 in seawater, fCO_2 , have been submitted to us by some investigators. However, often the fugacity is not clearly defined as to whether only the non-ideality arising from CO_2 - CO_2 molecular interactions is considered and/or that from CO_2 - H_2O interactions is also included. Because of these ambiguities, we have chosen not to list fCO_2 values. Since the mole fraction concentrations of CO_2 in equilibrated gas samples are also included in the reported data, we have computed pCO_2 using the reported temperature, pressure, and other data and listed in this report using the ideal gas law as explained earlier. Since fCO_2 values are always smaller than the corresponding pCO_2 values by 1 to 2 μ atm and the differences are large enough with respect to the precision of measurements and the mean global sea-air pCO_2 difference of about 10 μ atm, they should not be used interchangeably with pCO_2 .

Beginning with V2007 we added a column reporting the partial pressure of CO_2 in seawater in units of Pascals.

5. QUALITY CONTROL

Determination of surface water pCO_2 requires measurements for a number of parameters in addition to the concentration of CO_2 in the carrier gas equilibrated with seawater. With the broad range of

data sources and continued evolution of the measurement systems, it has not been possible to ensure that the observations contain all the necessary data elements with desired precisions. In some cases, $p\text{CO}_2$ or $f\text{CO}_2$ was reported without V_{CO_2} , sometimes with the pressure at the time of equilibration, sometimes not. Some files contained only the sea surface temperature and the $p\text{CO}_2$ at that temperature, but not the temperature and $p\text{CO}_2$ at equilibration. Ideally, the incoming file should contain the dried concentration of CO_2 in a parcel of air in equilibrium with seawater (V_{CO_2}), the temperature at the time of equilibration, and the equilibration pressure. When the pressure was not reported, we used the climatological value in the nearest box from the NCEP/NCAR Reanalysis II Project file for the month of the observation. We accepted data points that contained $p\text{CO}_2$ and sea surface temperature with or without the pressure.

Field data obtained in earlier years do not necessarily have all the required supporting measurements. For example, the temperatures of equilibration and water samples were recorded by hand at intervals of a few to several hours, and hence these values are often interpolated linearly with time between measurements. The salinity was measured only at hydrographic stations, and these values were interpolated between stations. When salinity was not measured during some expeditions, climatological values were assigned. Some data were unrecoverable and lost as a result of changes in computer systems (hardware and software). For the past decade, computer controlled systems for underway surface water $p\text{CO}_2$ measurements have been deployed widely, and more complete high quality data sets have been obtained. In constructing this data file, we exercised our personal judgment for accepting and rejecting data, especially those collected in earlier years. For more recent data sets, water flow rates through the equilibrator and the temperatures of equilibrator water are recorded for each $p\text{CO}_2$ measurement. They often served as important criteria for identifying satisfactory operation of the equilibrator. Measurements made at reduced or stopped water flow conditions were rejected, as were those made at unusually rapid changes in the temperature of the water in an equilibrator. CO_2 gas analyzers are commonly calibrated using three or more gas mixtures of different CO_2 concentrations. Those measurements made using only a single calibration gas mixture are subject to unspecified uncertainties, and hence are rejected.

All data points have been examined individually as they were integrated into this database. While not perfect, we have tried to edit out obvious problems, erring on the side of leaving in questionable ones. Considering differences in equilibrator designs, calibration methods and some interpolated parameters, we estimate that the uncertainty of the $p\text{CO}_2$ data presented in this data file is about $\pm 2.5 \mu\text{atm}$ on the average.

Seawater $p\text{CO}_2$ values that were computed using the alkalinity, total CO_2 concentration, and pH data are not included in this data file because of their large uncertainties and potential biases resulting from different dissociation constants of carbonic, boric and other acids used for the computations.

During many cruises, atmospheric CO_2 concentrations were measured concurrently with surface water $p\text{CO}_2$. However, we suspect that many of these measurements were contaminated by local sources (such as ship's exhausts). Since atmospheric CO_2 concentrations vary from one air mass to another, especially in the northern hemisphere, distinguishing local contamination from natural variability is difficult. Hence, we decided to omit the atmospheric CO_2 data from this file. We recommend that the atmospheric CO_2 concentration data listed in the GLOBALVIEW- CO_2 for computing the sea-air $p\text{CO}_2$ difference.

6. DATA SOURCES

The LDEO database lists more than 3 million surface ocean $p\text{CO}_2$ observations made since 1968. A large portion of the data is composed of observations from the continuous underway systems, such as those used aboard the National Science Foundation icebreakers *Nathaniel B. Palmer* and *Laurence B. Gould* operating primarily in the Southern Ocean, and the research ships operated by the Atlantic Oceanographic and Meteorological Laboratory and the Pacific Marine Environmental Laboratory of the National Oceanic and Atmospheric Administration. The database also includes the observations made during a number of major national and international oceanographic programs such as Geophysical Sections Experiment (GEOSECS), Joint Global Ocean Flux Study (JGOFS), World Ocean Circulation

Experiment (WOCE), Climate Variability (CLIVAR) Repeat Hydrography Project, Volunteer Observing Ships (VOS) Project and others, which were supported by the National Science Foundation, National Oceanic and Atmospheric Administration, and Department of Energy. A significant number of data have been contributed by international colleagues from many countries including Japan, Germany, France, UK, Iceland, Australia, Canada, the Netherlands, Norway, and others. Table 1 lists the major contributors for the database.

Table 1. List of data contributors to the global surface water pCO₂ LDEO database.

PI name*	Institution	Country
Thorarinn S. Arnarson	Marine Research Institute and University of Iceland	Iceland
Dorothee C. E. Bakker	School of Environmental Sciences, University of East Anglia	UK
Nicholas R. Bates	Bermuda Institute of Ocean Sciences	Bermuda
Richard Bellarby	Bjerknes Centre for Climate Research, University of Bergen	Norway
Wei-Jun Cai	University of Georgia	USA
Francisco Chavez	Monterey Bay Aquarium Research Institute	USA
David W. Chipman**	Lamont-Doherty Earth Observatory, Columbia University	USA
Cathy E. Cosca	Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration	USA
Bruno Delille	Universite de Liege, Liege	Belgium
Hein J. W. de Baar	Netherland Institute for Sea Research	Netherlands
Richard A. Feely	Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration	USA
Gernot Friederich	Monterey Bay Aquarium Research Institute	USA
John Goddard**	Lamont-Doherty Earth Observatory, Columbia University	USA
Burke Hales	College of Oceanic and Atmospheric Sciences, Oregon State University	USA
Mario Hoppema	Alfred Wegener Institute for Polar and Marine Research	Germany
Masao Ishii	Meteorological Research Institute	Japan
Truls Johannessen	Bjerknes Centre for Climate Research, University of Bergen	Norway
C. D. Keeling***	Scripps Institution of Oceanography, University of California San Diego	USA
Arne Körtzinger	Leibniz Institute of Marine Sciences	Germany
Nicolas Metzl	Laboratoire d'Océanographie et du Climat, Universite Pierre et Marie Curie	France
Takashi Midorikawa	Meteorological Research Institute	Japan
Ludger Mintrop	MARIANDA marine analytics and data	Germany
P. P. Murphy	Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration	USA
Timothy Newberger	Lamont-Doherty Earth Observatory, Columbia University	USA
Yukihiro Nojiri	National Institute for Environmental Studies	Japan
Jon Olafsson	Marine Research Institute and University of Iceland	Iceland
Are Olsen	Bjerknes Centre for Climate Research, University of Bergen	Norway
Christopher L. Sabine	Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration	USA
Ute Schuster	School of Environmental Sciences, University of East Anglia, Norwich	UK
Tobias Steinhoff	Leibniz Institute of Marine Sciences	Germany
Stewart C. Sutherland	Lamont-Doherty Earth Observatory, Columbia University	USA

Peter Salomeh	Scripps Institution of Oceanography	USA
Colm Sweeney	Earth System Research Laboratory, National Oceanographic and Atmospheric Administration	USA
Taro Takahashi	Lamont-Doherty Earth Observatory, Columbia University	USA
Bronte Tilbrook	Australian Commonwealth Scientific and Research Organization (CSIRO) Marine and Atmospheric Research	Australia
Rik Wanninkhof	Atlantic Oceanographic and Meteorological Laboratory, National Oceanographic and Atmospheric Administration	USA
Lee S. Waterman**	Scripps Institution of Oceanography, University of California San Diego	USA
Andrew Watson	School of Environmental Sciences, University of East Anglia	UK
Ray F. Weiss	Scripps Institution of Oceanography, University of California San Diego	USA
C. S. Wong	Institute of Ocean Sciences	Canada
H. Yoshikawa-Inoue	Graduate School of Environmental Earth Science, Hokkaido University	Japan

*The PI names are given in the alphabetical order.

**Retired

***Deceased

7. DATA LISTING

This NDP consists of two files: the file called “LDEO_Database_V2009.txt” contains all the numerical data, and the file “LDEO_Database_Metadata_V2009.csv” contains information on the data source, credit, institution, etc. The data elements in “LDEO_Database_V2009.txt” and their units are listed in Table 2; and those in “LDEO_Database_Metadata_V2009.csv” are explained in Table 3. Detailed cruise documentation (such as names of ship and ports and dates for departure and arrival) may be obtained directly from the respective PI’s.

Table 2. Data elements listed in the master data file “LDEO_Database_V2009.txt”

CRUISE_ID*	Internal LDEO Cruise Number
STN*	Station number assigned in the LDEO File
LAT	Latitude in decimal degrees (North is positive)
LON	Longitude in decimal degrees (East is positive)
MONTH/DAY/YEAR	Date
JDATE	Julian Date in decimal notation. Convention is 0001 UTC 1 Jan = 1.0
VCO2_SW**	Mole fraction concentration of CO ₂ (ppm) in dried air
TEMP_PCO2	Temperature at which pCO ₂ was measured in °C
SST	Sea Surface Temperature in °C
SSS	Sea Surface Salinity
PCO2_SST	Partial Pressure of CO ₂ in seawater (in units of microatmospheres) at the temperature in the SST column
PCO2_SSTPA	Partial Pressure of CO ₂ in seawater (in units of Pascals) at the temperature in the TEMP column
PCO2_TEQ	Partial Pressure of CO ₂ in seawater (in units of microatmospheres) at the temperature in theTEMP_PCO2 column. This is ordinarily the value that is actually measured
EQ_PBARO	Pressure in the equilibration vessel in units of millibars

SHIPPBARO	Barometric pressure in the outside air from the ship's observation system in units of millibars
-----------	---

*Cross reference fields to the internal LDEO file name in case problems are discovered

**Missing data have the value -999.9

Table 3. Data elements listed in the metadata file “LDEO_Database_Metadata_V2009.csv”

CruiseID	Internal LDEO File Name
LEG	Leg Number. This is an arbitrary designation in many files because of our limit of four characters for a station number. For surface underway files that normally have many more than 9,999 observations we have broken the file into “legs.”
SHIP/EXPERIMENT	The name of the ship or other platform used, and experiment, project
CRUISE_NAME	Cruise name
OBSERVER	A notation of the person making the observation or responsible for running the collection system
DEPARTURE_PORT	Port of Departure
DEPARTURE_DATE	Date of Departure
ARRIV_EPORT	Port of Arrival
ARRIV_EDATE	Date of Arrival
COMMENT*	Air data source and general information

*Additional information may be available for a particular file if needed.

8. HOW TO OBTAIN THE DATA AND DOCUMENTATION

The LDEO database NDP-088(V2009) is available free of charge from CDIAC. The complete documentation and data can be obtained from the CDIAC oceanographic web site (http://cdiac.ornl.gov/oceans/LDEO_Underway_Database/).

Contact information:

Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, Tennessee 37831-6335
USA
Telephone: (865) 574-3645
Telefax: (865) 574-2232
E-mail: cdiac@ornl.gov
Internet: <http://cdiac.ornl.gov/>

9. ACKNOWLEDGEMENTS

Many national and international investigators contributed their observations to this database. ORNL gratefully acknowledges the efforts of investigators and supporting staff at sea and on land. Richard A. Feely [Pacific Marine Environmental Laboratory/National Oceanographic and Atmospheric Administration (PMEL/NOAA)] and Rik Wanninkhof [Atlantic Oceanographic and Meteorological Laboratory (AOML) /NOAA] offered encouragement in this task; this was appreciated. . We gratefully acknowledge that the continued support from the Office of Global Programs of the National Oceanic and Atmospheric Administration has made this compilation possible. The field study of T. Takahashi and his associates have been supported by the National Science Foundation, the National Oceanic and Atmospheric Administration, Department of Energy, Comer Science and Education Foundation, Ford Motor Company and EXXON Research and Engineering Company.

10. REFERENCES

- Baker D. F., R. M. Law, K. R. Gurney, P. Rayner, P. Peylin, A. S. Denning, P. Bousquet, L. Bruhwiler, Y.-H. Chen, P. Ciais, I. Y. Fung, M. Heimann, J. John, T. Maki, S. Maksyutov, K. Masari, M. Prather, B. Pak, S. Taguchi, and Z. Zhu. 2006. TransCom 3 inversion intercomparison: Impact of transport model errors on the interannual variability of regional CO₂ fluxes, 1988-2003. *Global Biogeochem. Cycles*, 20, GB1002, doi. 10.1029/2004GB2002439.
- Bender, M.L., D.T. Ho, M.B. Hendricks, R. Mika, M.O. Battle, P.P. Tans T.J. Conway, B. Sturtevant, and N. Cassar. 2005. "Atmospheric O₂/N₂ changes, 1993–2002: Implications for the partitioning of fossil fuel CO₂ sequestration," *Global Biogeochemical Cycles* 19:GB4017, doi:10.1029/2004GB002410.
- Broecker, W.S. and T. Takahashi. 1966. „Calcium carbonate precipitation on the Bahama Banks,“ *Journal of Geophysical Research* 71:1575–1602.
- Chavez, F. and T. Takahashi. 2007. Coastal oceans, Chapter 15, in "The First State of the Carbon Cycle Report (SOCCR): North American Carbon Budget and Implications for the Global Carbon Cycle". A report by the U.S. Climate Change Science Program and the Subcommittee on Global Change Research [King, A.W. L. Dilling. G.P. Zimmerman, D.M. Fairman, R.A. Houghton, G.H. Marland, A.Z. Rose, and T.J. Wilbanks (eds.)] National Ocean and Atmospheric Administration, Climate Program Office, Silver Spring, MD, USA, pp. 83–92.
- GLOBALVIEW-CO2: 2006. *Cooperative Atmospheric Data Integration Project—Carbon Dioxide*. CD-ROM, NOAA CMDL, Boulder, Colorado (also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/co2/GLOBALVIEW).
- Gruber, N., and C. D. Keeling. 2001. An improved estimate of the isotopic air-sea disequilibrium of CO₂: Implications for the oceanic uptake of anthropogenic CO₂. *Geophys. Res. Lett.*, 28(3), 555–558, doi:10.1029/2000GL011853.

- Gruber, N. and J.L. Sarmiento. 2002. "Large-scale biogeochemical-physical interactions in elemental cycles." In *The Sea*, Vol. 12:337–99. John Wiley & Sons, New York.
- Gruber, N., M. Gloor, S. E. Mikaloff Fletcher, S. C. Doney, S. Dutkiewicz, M. Follows, M. Gerber, A. R. Jacobson, F. Joos, K. Lindsay, D. Menemenlis, A. Mouchet, S. A. Müller, J. L. Sarmiento, and T. Takahashi. 2009. Oceanic sources, sinks, and transport of atmospheric CO₂. *Glob. Biogeochem. Cycles.*, 23, GB1005, doi:10.1029/2008GB003349.
- Keeling, C. D. 1965. Carbon dioxide in surface waters of the Pacific Ocean, 2, Calculation of the exchange with the atmosphere. *Journal of Geophysical Research*, 70:6099–102.
- Keeling, C. D., N. W. Rakestraw and L. S. Waterman. 1965. Carbon dioxide in surface waters of the Pacific Ocean, 1, Measurements of the distribution. *Journal of Geophysical Research*, 70:6087–98.
- Keeling, C. D. 1968. Carbon dioxide in surface waters, 4. Global distribution. *Journal of Geophysical Research*, 73:4529–4542.
- Keeling, C. D. and L.S. Waterman. 1968. Carbon dioxide in surface waters, 3. Measurements on Lusiad Expedition 1962-1963. *Journal of Geophysical Research*, 73:4529–42.
- Keeling, R.F., S.C. Piper, and M. Heinmann. 1996. "Global and hemispheric CO₂ sinks deduced from changes in atmospheric O₂ concentration," *Nature* 381:218–21.
- Keeling, C. D., N.W. Rakestraw, and L.S. Waterman. 1965. "Carbon dioxide in surface waters of the Pacific Ocean, 1, Measurements of the distribution," *Journal of Geophysical Research* 70:6087–98.
- Manning, A. C. and R. F. Keeling. 2006. Global oceanic and land biotic carbon sinks from the Scripps atmospheric oxygen flask sampling network. *Tellus B* 58:95–116.
- Murray, C. N. and J. P. Riley. 1971. The solubility of gases in distilled water and seawater - IV. Carbon dioxide. *Deep-Sea Res.*, 18:533–541.
- Matsumoto, K. et al. 2004. Evaluation of ocean carbon cycle models with data-based metrics. *Geophys. Res. Lett.*, 31, LO7303, doi:10.1029/2003GL018970.
- Metzl, N. 2009. Decadal increase of oceanic carbon dioxide in the Southern Indian Ocean surface waters (1991–2007). *Deep-Sea Res. II*, doi:10.1016/j.dsr2.2008.12.007.
- Patra, P. K., Gurney, K. R., Denning, A. S., Maksyutov, S., Nakazawa, T., Baker, D., Bousquet, P., Bruhwiler, L., Chen, Y.-H., Ciais, P., Fan, S., Fung, I., Gloor, M., Heinmann, M., Higuchi, K., John, J., Law, R. M., Maki, T., Pak, B.C., Peylin, P., Prather, M., Rayner, P. J., Sarmiento, J., Tauchi, S., Takahashi, T. and Yuen, C.- W. 2006. Sensitivity of inverse estimation of annual mean CO₂ sources and sinks to ocean-only sites versus all-sites observational networks. *Geophys. Res. Lett.*, 33, LO5814, doi:10.1029/2005GL025403.

- Quay, P., R. Sommerup, T. Westby, J. Sutsman, and A. McNichol. 2003. "Changes in the $^{13}\text{C}/^{12}\text{C}$ of dissolved inorganic carbon in the ocean as a tracer of anthropogenic CO_2 uptake." *Global Biogeochemical Cycles* 17, No. 1:DOI 10.1029/2001GB001817.
- Sarmiento, J. L., P. Monfray, E. Maier-Reimer, O. Aumont, R.J. Murnane, and J.C. Orr. 2000. "Sea-air CO_2 fluxes and carbon transport: A comparison of three ocean general circulation models." *Global Biogeochemical Cycles* 14:1267–81.
- Sabine, C.L., R. A. Feely, N. Gruber, R. M. Key, K. Lee, J. L. Bullister, R. Wanninkhof, C. S. Wong, D. W. R. Wallace, B. Tilbrook, F. J. Millero, T.-H. Peng, A. Kozyr, T. Ono, A. F. Rios. 2004. The Oceanic Sink for Anthropogenic CO_2 . *Science* 305(5682):367-371.
- Takahashi, T. 1961. "Carbon dioxide in the atmosphere and in the Atlantic Ocean water," *Journal of Geophysical Research* 66:477–94.
- Takahashi, T., J. Olafsson, J. Goddard, D.W. Chipman, and S.C. Sutherland. 1993. "Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: A comparative study," *Global Biogeochemical Cycles* 7:843–78.
- Takahashi, T., R.A. Feely, R. Weiss, R. Wanninkhof, D.W. Chipman, S.C. Sutherland, and T. Takahashi. 1997. "Global air-sea flux of CO_2 : an estimate based on measurements of sea-air pCO_2 difference," *Proc. Nat. Acad. Sci.*, 94:8292–99.
- Takahashi, T., S.C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, B. Tillbrook, N. Bates, R. Wanninkhof, R.A. Feely, C.L. Sabine, J. Olafsson, and Y. Nojiri. 2002. "Global sea-air CO_2 flux based on climatological surface ocean pCO_2 , and seasonal biological and temperature effects," *Deep-Sea Research II*, 49:1601–22.
- Takahashi, T., S. C. Sutherland, R. Wanninkhof, C. Sweeney, R. A., Feely, D. W. Chipman, B. Hales, G. Friederich, F. Chavez, C. Sabine, A. Watson, D. C. E. Bakker, U. Schuster, N. Metzl, H. Yoshikawa-Inoue, M. Ishii, T. Midorikawa, Y. Nojiri, A. Kortzinger, T. Steinhoff, M. Hoppema, J. Olafsson, T. S. Arnarson, B. Tillbrook, T. Johannessen, A. Olsen, R. Bellerby, C. S. Wong, B. Delille, N. R. Bates, and H. J. W. de Baar. 2009. Climatological mean and decadal change in surface ocean pCO_2 and net sea-air CO_2 flux over the global oceans. *Deep-Sea Res. II*, 56, 554-577, doi:10.1016/j.dsr2.2008.12.009.
- TRENDS on line. 2006. "A Compendium of Data on Global Change. Carbon Dioxide Information and Analysis Center," Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN <http://cdiac.ornl.gov/trends/co2/contents/html>).
- Wanninkhof, R. and K.Thoning. 1993. Measurement of fugacity of CO_2 in surface water using continuous and discrete sampling methods. *Marine Chem.*, 44:189–204.
- Waterman, L. S., P. P. Tans, T. Aten, C. D. Keeling, and T. A. Boden. 2006-a. Surface water and atmospheric underway carbon dioxide data obtained during Downwind (1957) expedition of Scripps Institution of Oceanography. Scripps Institution of Oceanography, Univ. California San Diego, La Jolla, CA http://scrippsco2.ucsd.edu/data/seawater_pco2/pco2_downwind_1957.csv

- Waterman, L. S., P. P. Tans, T. Atten, C. D. Keeling, and T. A. Boden. 2006-b. Surface water and atmospheric underway carbon dioxide data obtained during " Monsoon (1961) expedition of Scripps Institution of Oceanography. Scripps Institution of Oceanography, Univ. California San Diego, La Jolla, CA
http://scrippsco2.ucsd.edu/data/seawater_pco2/pco2_monsoon_1961.csv
- Waterman, L. S., P. P. Tans, T. Atten, C. D. Keeling, and T. A. Boden. 2006-c. Surface water and atmospheric underway carbon dioxide data obtained during Lusiad (1962) expedition of Scripps Institution of Oceanography. Scripps Institution of Oceanography, Univ. California San Diego, La Jolla, CA
http://scrippsco2.ucsd.edu/data/seawater_pco2/pco2_lusiad_1962.csv
- Waterman, L. S., P. P. Tans, T. Atten, C. D. Keeling, and T. A. Boden. 2006-d. Surface water and atmospheric underway carbon dioxide data obtained during Lusiad (1963) expedition of Scripps Institution of Oceanography. Scripps Institution of Oceanography, Univ. California San Diego, La Jolla, CA
http://scrippsco2.ucsd.edu/data/seawater_pco2/pco2_lusiad_1963.csv
- Weiss, R. F. 1974. Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chem.*, 2:203–215.
- Weiss, R. F. and B. A. Price. 1980. Nitrous oxide solubility in water and seawater. *Marine Chem.*, 8:347–359.

